Utilization of Waste of Enzymes Biomass as Biosorbent for the Removal of Dyes from Aqueous Solution in Batch and Fluidized Bed Column

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The biosorption performance of both batch and liquid-solid fluidized bed operations of dead fungal biomass type (Agaricusbisporus) for removal of methylene blue from aqueous solution was investigated. In batch system, the adsorption capacity and removal efficiency of dead fungal biomass were evaluated. In fluidized bed system, the experiments were conducted to study the effects of important parameters such as particle size (701-1400µm), initial dye concentration(10-100 mg/L), bed depth (5-15 cm) and solution flow rate (5-20 ml/min) on breakthrough curves. In batch method, the experimental data was modeled using several models (Langmuir,Freundlich, Temkin and Dubinin-Radushkviechmodels) to study equilibrium isotherms, the experimental data followed Langmuir model and the results showed that the maximum adsorption capacity obtained was (28.90, 24.15, 21.23 mg/g) at mean particle size (0.786, 0.935, 1.280 mm) respectively. In Fluidized-bed method, the results show that the total ion uptake and the overall capacity will be decreased with increasing flow rate and increased with increasing initial concentrations, bed depth and decreasing particle size.

Keywords: Methylene blue dye; Biosorption; fungal biomass; Batch experiments, Fluidized bed column; Equilibrium isotherms; breakthrough curves.

The pollution of water is one of the main environmental problems facing our planet in the present days due to the increase in the waste of the industrial activities which are often discharged into nature without suitable treatments. Dyes are not biodegradable and their presence in water leads to bioaccumulation in living organisms causing health problems in animals, plants and human beings which require several steps of treatment before draining them into the environment [1]. Dyes are colored materials which can be used in leather, food, paper, textile, printing, and plastics industries. Several methods have been used to remove dyes from the influent water like reverse osmosis, membrane separation, chemical oxidation, coagulation, activated sludge process, and biological treatments; however, the most efficient used method is the adsorption/biosorption method [2, 3].

The adsorption/ biosorption process has been widely used in wastewater treatments for several reasons such as; it has a simple operating procedure, a relatively small operating space, a capacity for large treatment volumes of effluent, has significant yields, has a large range of feed concentrations, a regeneration of biosorbent, fairly low cost with high efficiency, and an easy scaling–up [4, 5]. The decolorization of dyes requires high attention from authorities due to their toxicity, carcinogenic and mutagenic behavior [6]. The methylene blue (MB) was chosen for this study because of its known strong adsorption to solids. MB is the most commonly used material for dying cotton, wood, and silk with a molecular weight of 373.9 that corresponds to MB hydro chlorine with three groups of water [7].

At present, physical and chemical methods are widely used as a treatment process for removing dyes from wastewater, but these methods are not cost-effective or environmentally friendly. As a result, an alternative technology for wastewater treatment has become a necessity for a composite knit industry. Biological processes using microbial systems may provide an alternative to the existing physical/chemical technologies since they are more cost-effective, environmentally friendly, and do not produce large quantities of sludge [8, 9]. Biosorption, which is a process that utilizes biological materials as adsorbents, has been studied by several researchers as an alternative technique to conventional methods for removing heavy metals and dyes from wastewater [10-13].

Fungal systems appear to be most appropriate as a biological agent in the treatment of colored and metallic effluents. In recent years, several biosorbents have been identified as possessing good dye-binding capabilities [14-17]. The main objective of this study is to study the effects of equilibrium adsorption isotherms on the characteristic of mass transfer coefficient related to the biosorption process. We also aim to evaluate the performance of the fluidized -

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-bed system for the removal of methylene blue colored materials from wastewaters using dead fungal biomass type (Agaricusbisporus) as a low-cost biosorbent with different parameters of the process such as particle size of biosorbent, initial concentration and flow rate of influent solution.

Experimental part

Materials and methods

Adsorbate materials

Methylene Blue ($C_{16}H_{18}ClN_3S.2HO$; molecular weight: 319.86) is cationic dye purchased from Fisher Scientific. The MB was chosen in this study because of its known strong adsorption on solids. The maximum adsorption wavelength of this dye is 661 nm. The structure of MB is shown in figure 1.

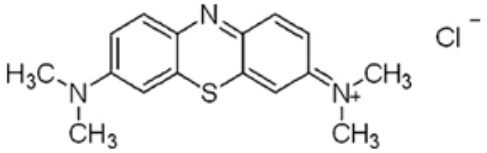

Fig. 1. Chemical structure of Methylene Blue dye

Biosorbent materials

Waste of fungi (WF) can be obtained at the end of harvested of mushroom type (*White Agaricus Bisporus*) from industrial farms. This type of mushroom was cultured at the north-west of Iraq. The WF was grounded, screened to a required size, washed several times by potable water and distilled water to ensure clean biomass from impurities before using in experiments, then dried for 48 h in an oven at 60 °C to ensure removing the moisture from biomass and kept in a desiccators.

A dead cell WF was sieved through a [1400-1180; 992-883 and 883-701] µm diameter mesh by using successive sieves (Restech, ASTM-E11, Germany). For non-spherical particles, the particle diameter (d_p) is defined as the equivalent diameter of a spherical particle with the same volume. As an approximation, the particle diameter (d_p) may be calculated from the geometric mean of the two consecutive sieve openings without introducing serious errors. The geometric mean diameter is given by $d_{gm} = (d_1 d_2)^{1/2}$, where d_1 is the diameter of the lower sieve on which the particles are retained, d_2 is the diameter of the upper sieve through which the particles pass. The mean particle diameter of the WF used is 1.28, 0.935 and 0.786 mm respectively. Figures 2 and 3 show the dried biomass before and after treatment.

Fig. 2. Untreated WF biomass

Fig. 3. A sample of treated **WF**

Table 1 shows the physical properties of the WF used in this work.

Table 1
PHYSICAL PROPERTIES OF WF

Raw material	WF
Bulk density, kg/m^3	436.11
BET surface area, m^2/g	3,474
Real density, Kg/m^3	2139.6
Particle porosity %	79.62
Bed porosity %	68.31
Ash Content, %	Below 5
Mean particle sizes, mm	1.28, 0.935, 0.786

Preparation of stock solutions

Stock solution of methylene blue was prepared from methylene blue powder, where 1.00 g of powder was diluted with deionized water in a 1000 ml volumetric flask to prepare the stock solution with concentration of 1000 mg/L. Working solutions of different concentrations (10-100 mg/L) were prepared by further dilutions.

Dye concentration analysis

Standard curves were developed through the measurement of absorbance of the dye solutions at maximum wavelength of λ=661 nm by UV/Visible Spectrophotometer (Shimadzu model UV-160A ultraviolet/visible spectrophotometer).

Batch biosorption experiments

Batch experiments were carried out in 10 bottles of 250 ml conical flasks containing desired weight (0.3 g) of dead fungal biomass and 50 ml of aqueous methylene blue solution with different concentrations ranging from 10 to100 mg/L. The initial desired pH value of the solution (6.0) was adjusted by adding NaOH or HCl. The flasks were shacked (at room temperature 298K) for 3 h to attain equilibrium. Preliminary investigations showed that the biosorption process of each studied ion was completed after 40 min. The suspension obtained was centrifuged and filtered to separate the solid from the liquid phase. Clear liquid solution of 10 ml was used to measure the initial and final concentrations by using UV-VIS spectrophotometer.

All experiments were duplicated and only the mean values were reported, the maximum deviation observed was less than$\pm$4%.

The adsorbed amount M. B. dye can be calculated by the following equation:

$$q_e = (C_o - C_e) \times \frac{V}{w} \quad (1)$$

where C_o and C_e are the initial and equilibrium concentrations of dye (mg/L) respectively, V is the volume of dye solution (L) and w is the amount of adsorbent used (g). To determine the percentage of dye removal, the following equation (2) is used:

$$\%\ Removal = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

Fluidized-bed experiments

A glass column made of cylinder (1) of 5 cm diameter and 60 cm height was used as the fluidization column (fig. 4). A dye solution of known concentration was made in 100 L capacity glass storage tank (2). This solution was then pumped by a 1 hp pump (6) through the dead fungal biomass bed across a Rota meter (3). The flow rate to the fluidized bed was kept constant by adjusting the valve (5) of the bypass line and the manually controlled valve (4) of the main flow path. Samples were collected at a definite time interval from the exit point (8) and exit solution was stored and then drained out from the effluent tank (7). The storage tank (2) and glass cylindrical column were then washed to set up for a new run. A series of experiments were performed by changing different parameters of the fluidized bed system.

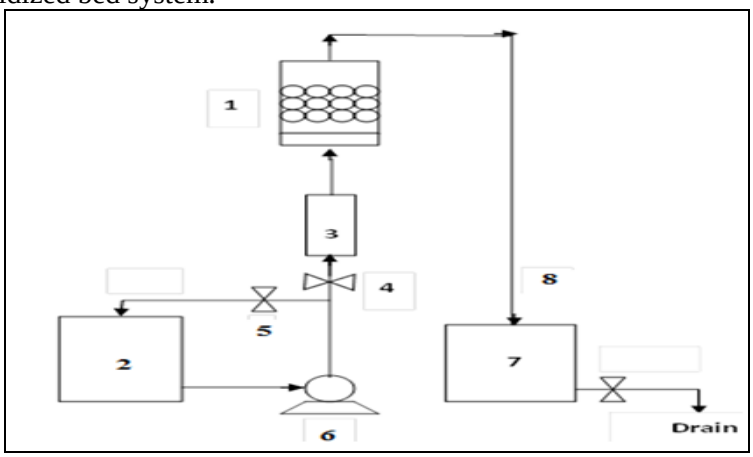

Fig. 4. Schematic diagram of the up-flow fluidized bed bioreactor: 1- glass column; 2- glass storage tank; 3- Rota meter; 4- manually controlled valve; 5- valve; 6- hp pump; 7- effluent tank; 8- exit point

Results and discussions

Effect of pH

The biosorption capacity was affected by initial pH solution which plays an important role in the whole biosorption process of MB. For this research, 0.3 g dose from biosorbent with initial concentration of MB solution is 50 mg/L at

25C and contact time 180 min. The range of pH used is 2-10. The results are shown in figure (5). At pH 2, minimum dye removal adsorbed. When pH increases from 2 to 7, the percentage removal and uptake capacity will be increased from 36.4% to 99.5% (7.28 to 19.9 mg/g). The maximum percentage removal and uptake capacity are found at pH 6, so pH 6 is selected for further experiments, beyond pH 6, there was no significant change in the amount adsorbed by further increased. This phenomenon can be explained; generally, the charge of cationic dye dissolved in aqueous solution is positive. When pH value around 2 the adsorbent surface have positive charges due to adsorbing H^+ ions, which prevents the adsorption of cationic dye onto the adsorbent surface due to electrostatic repulsion and the competition between H^+ ions and cationic dye for the adsorption sites [19].When initial pH increased, the number of negatively charged surface sites on the adsorbent increased, which may be lead to an increase in the adsorption of cationic dye due to the electrostatic attraction [20]. At higher pH, the surface of the adsorbent becomes negatively charged and there exists a strong electrostatic attraction of dye cations with the adsorbent leading to the increased adsorption [21].

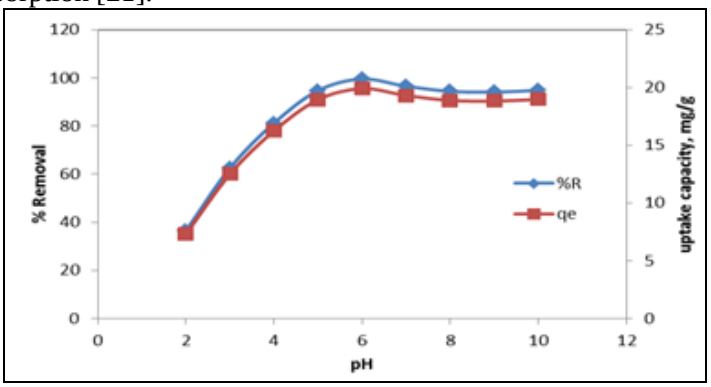

Fig. 5. Effect of *p*H on % removal and biosorption capacity of MB by WF

Effect of biosorbent dose

The effect of biosorbent dose on MB adsorption is shown in figure (6) by varying the biosorbent dose from 0.05 to 1.0 g at conditions of a particle size of 953 µm, 50 mg/L dye concentration, and an agitation rate of 200 rpm at ambient temperature. Percentage removal of dye increases rapidly from 41.2 to 99.8% with a raise in biosorbent mass from 0.05 to 0.35 g; this is due to the increasing in surface area of the biosorbent and the large number of vacant sites which leads to more biosorption. Also from the same figure, it can be seen that the uptake capacity of MB biosorbed per gram of biosorbent has decreased from 20.6 to 7.2 mg/g; this decrease in biosorption capacity q_e is basically due to the remaining unsaturated sites during the biosorption process [22].

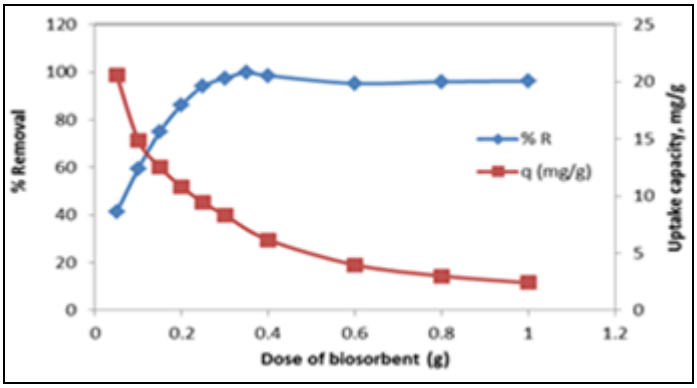

Fig. 6. Effect of biosorbent dose on % removal and biosorption capacity of MB WF

Effect of contact time

The effect of contact time on biosorption process was studied using 50 mg/L as an initial dye concentration with biosorbent mass of 0.3 g at pH 6 and an agitation speed of 200 rpm over a period of time of 180 minutes at ambient temperature. Figure (7) shows that the adsorption capacity and removal efficiency for MB has increased rapidly within the first 40 minutes, and then gradually slowed as the equilibrium is attained. At the time of 40 minutes, the maximum adsorption capacity and percentage removal were 33.06 mg/g and 99.2% respectively. This phenomenon is related to a large number of vacant active surface sites on biosorbent surface that are available at the initial stage of the biosorption process. The rapid attachment of dye molecules to the surface of the biosorbent leads to an increase in the driving force of the concentration gradient between adsorbate in the solution and the adsorbate-adsorbent interaction causing a higher diffusion of MB from the bulk solution to the biosorbent sites [23]. The remaining vacant sites are less available for adsorption with time resulting in reduced diffusion gradient and hence the rate of sorption has

decreased with time until it reached equilibrium at 40 minutes. One hour is used throughout the study to ensure that the equilibrium was reached.

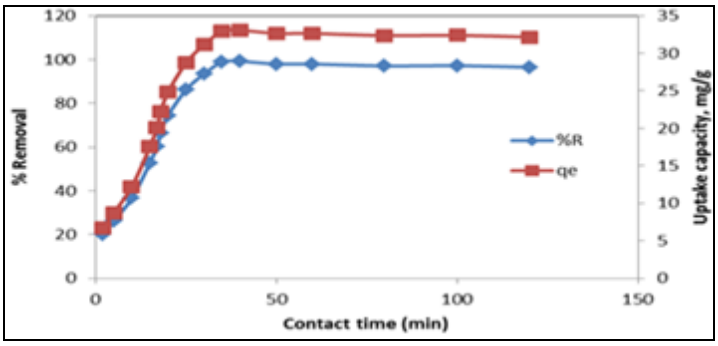

Fig. 7. Effect of contact time on % removal and biosorption capacity of MB by WF

Biosorption isotherms

Adsorption isotherm shows the distribution of molecules between the liquid phase and the solid phase at equilibrium stage. Several isotherm models such as Langmuir, Freundlich, Temkin and Dubinin-Radushkviech (D-R) were used in this work to describe the equilibrium data.

Langmuir isotherm model

The Langmuir adsorption model assumes that the adsorption of MB on a homogeneous surface of fungi, as a biosorbent material, take place without any interaction between the molecules of the adsorbate-adsorbent [24]. Langmuir isotherm model can be expressed as**:**

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (3)$$

The linear form of the Langmuir adsorption model is

$$\frac{C_e}{q_e} = \frac{1}{b * q_m} + \frac{1}{q_m} C_e \quad (4)$$

where C_e (mg/L) is the concentration of MB dye at equilibrium, q_e (mg/g) is the amount of MB dye adsorbed onto biosorbent at equilibrium, q_m (mg/g) is the maximum monolayer capacity of the adsorbent and b (L/mg) is the Langmuir isotherm constant related to the energy of adsorption. When plotting C_e/q_e versus C_e, it gives a straight line (fig. 8), the slope and intercept can be used to find the values of q_m and b respectively. As shown in table 2 , the values of R^2 at different particle sizes were determined to be in the range of 0.9724 to 0.9967 implies that the Langmuir isotherm provides a good mathematical fit to the isotherm data which can be seen clearly in figure (12).

In order to characterize the essential features of the Langmuir isotherm, the dimensionless constant separation factor R_L can be used to determine the nature shape of the isotherm. R_L is defined as;

$$R_L = \frac{1}{1 + b C_o} \quad (5)$$

where b is the Langmuir constant (L/mg) and C_o is the initial MB concentration (mg/L).

As presented in table 2, the values of R_L ranging between 0 and 1, that means favourable adsorption.

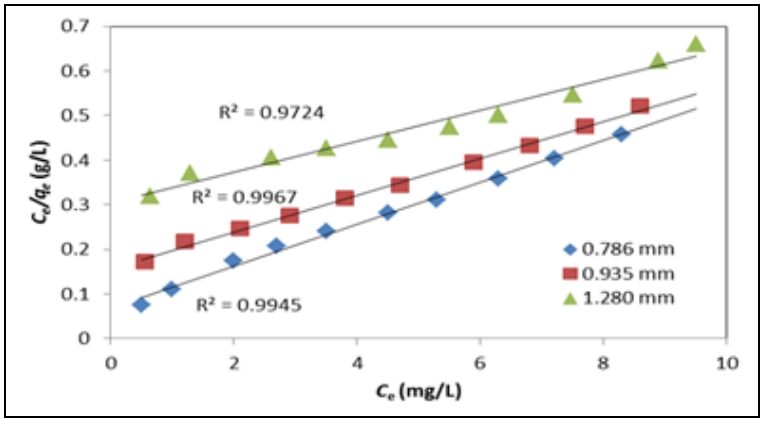

Fig. 8. Langmuir biosorption isotherm for biosorption MB onto WF

Freundlich isotherm model

The Freundlich isotherm model is based on adsorption on a heterogeneous surface; it assumes heterogeneous surface energies in which energy varies as a function of the surface coverage. The Freundlich isotherm relationship is an exponential function which takes the form:

$$q_e = K_f (C_e)^{1/n} \quad (6)$$

where q_e (mg/g) and C_e (mg/L) are the uptake capacity and concentration of the adsorbate at equilibrium respectively. K_f (mg/g) $(L/mg)^{1/n}$ and n are constants related to capacity and intensity of adsorption respectively [25]. The linearized form of Freundlich can be written as follows:

$$ln\, q_e = lnk_f + \frac{1}{n} lnC_e \quad (7)$$

Figure 9 shows the plot of ln C_e versus $ln\ q_e$ and K_f and n can be determined from the slope and intercept of the plot. From table 2, it can be seen that the values of R^2 for Freundlich isotherm is lower than that obtained for the Langmuir isotherm which confirms that the experimental data can be well described by Langmuir model. Also from the values of n, it is found that $n \geq 1.3$, which illustrates that MB is favorably adsorbed onto WF[26].

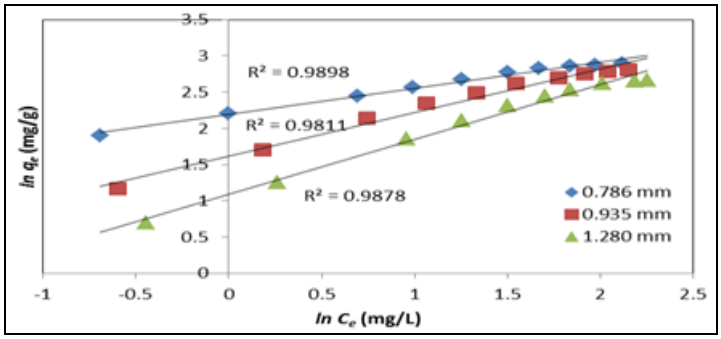

Fig. 9. Freundlich biosorption isotherm for biosorption MB onto WF

Temkin isotherm model

This type of adsorption isotherm model is based on the assumption that the heat of adsorption of all molecules in the layer will decrease linearly with coverage due to interaction between the adsorbate and the adsorbent [27]. The general form of Temkin isotherm model is:

$$q_e = \frac{RT}{b} \ln(K_T C_e) \quad (8)$$

The linear form of equation (8) is

$$q_e = \frac{RT}{b} (lnK_T + lnC_e) = A + B * lnC_e \quad (9)$$

where b is a factor related to the heat of adsorption and K_T is Temkin equilibrium constant (L/mg). The values of K_T and b can be calculated from the intercept and slope of equation (9) by plotting q_e versus lnC_e (fig. 10). The values of correlation coefficients R^2 are slightly lower compared with Langmuir and Freundlich isotherms which indicate a non-uniform distribution of binding energy arising due to the interaction of the dye molecules.

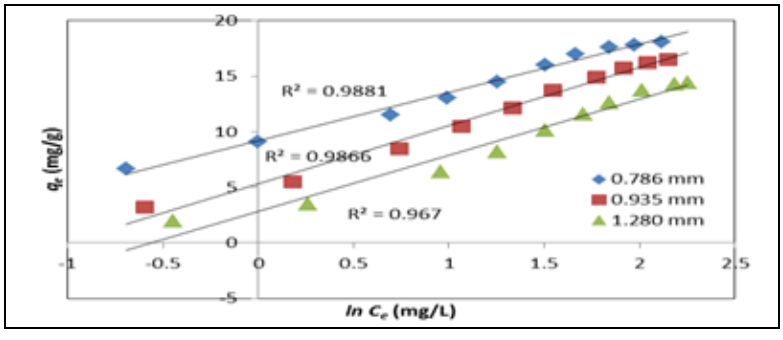

Fig. 10. Temkin biosorption isotherm for biosorption MB onto WF

Dubinin-Radushkviech isotherm (D-R isotherm)

The D-R isotherm model is used to estimate the characteristic porosity of the biosorbent and apparent energy of adsorption [28]. Assuming a heterogeneous surface, this module is usually applied to distinguish whether the adsorption is physical or chemical by evaluating the type of interaction between MB dye and WFas biosorbent. The D-R isotherm equation is:

$$q_e = q_m \exp(-\beta \varepsilon^2) \quad (10)$$

The linear form of D-R isotherm can be expressed as follows:

$$ln q_e = ln q_m - \beta \varepsilon^2 \quad (11)$$

where q_e is the equilibrium amount of MB dye adsorbed on WF(mg/g), q_m is the Dubinin-Radushkevich monolayer capacity (mol/g), β is a constant related to sorption energy (mol^2 / J^2), and ε is the polanti potential, which can be calculated as follows:

$$\varepsilon = RT ln(1 + \frac{1}{C_e}) \quad (12)$$

where C_e is the equilibrium constant of MB dye (mg/L), R is the gas constant (8.314 J/mol K), and T is the temperature in K.

The free energy E (kJ/mol) can be calculated from constant β using the following relationship:

$$E = \frac{1}{\sqrt{-2\beta}} \quad (13)$$

The magnitude of E can be related to the reaction mechanism. The adsorption process will be chemisorption when the value of E is between 8 and 16 kJ/mol, while for values of $E < 8$ kJ/mol, the sorption process is of physical nature [29].

By plotting lnq$_e$ against ε^2 gives a straight line to obtain q_m and β from the intercept and slope respectively as shown in figure 11, The D-R parameters q_m, β, ε, E and R^2 are presented in Table 2. The values of mean free energy E of sorption in all cases are below 8 kJ/mol, which means that the adsorption process is a physical process. Finally from Table 2, the Langmuir isotherm model shows the best fit compared to other isotherm models used in this study under all the experimental conditions. The results show that the adsorption of MB dye is a monolayer on the WFused as a biosorbent.

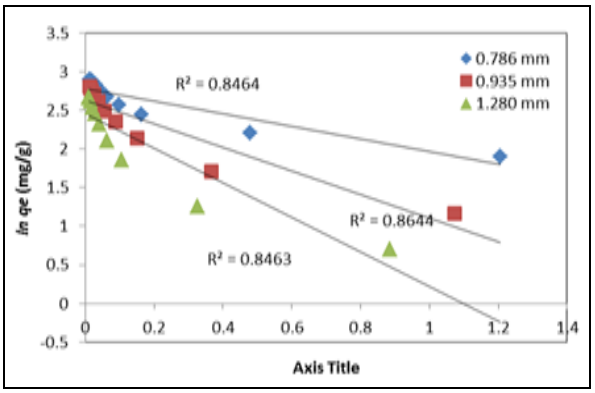

Fig. 11. Dubinin-Radushkviech biosorption isotherm for biosorption MB onto WF fungi

Table 2
ISOTHERM PARAMETERS FOR M.B. IONS ADSORBED ONTO WF BIOMASS WITH CORRELATION COEFFICIENT

Model	Parameters	Value		
Langmuir Eq. (8)	d_{pm}(mm)	0.786	0.935	1.280
	q_m(mg/g)	28.90	24.15	21.230
	b(1/mg)	0.1140	0.2643	0.6950
	R_L	0.1835	0.0934	0.0392
	R^2	0.9724	0.9967	0.9945
Freundlich Eq. (11)	K_f(mg/g)(L/mg)$^{1/n}$	2.9766	5.0339	8.9495
	n	1.3208	1.6539	2.7517
	R^2	0.9878	0.9866	0.9898
Temkin Eq. (13)	K_T(L/g)	1.7594	2.7744	8.3449
	B	5.0479	5.2229	4.3390
	R^2	0.9670	0.9866	0.9881
Dubinin-Radushkeich Eq. (15)	$\beta(\frac{mol^2}{kJ^2})$	-2.2327	-1.5233	-0.8119
	q_m(mg/g)	11.6034	13.9015	16.0787
	E (kJ/mol)	0.4732	0.5729	0.7847
	R^2	0.8463	0.8644	0.8464

Effect of particle size

Figures 12-14 show the effect of particle size on uptake removal of MB onto WF biomass. Two facts are shown here, the first is that the Langmuir isotherm model shows the best fit to experimental data compared with other isotherm models, and the second fact indicates that large amount from MB ions are removed from aqueous solution when the mean particle size of biosorbent is small (0.786 mm) compared with the other two mean particle sizes (0.935 mm and 1.280 mm) respectively. This is due to the availability of large surface area of the biosorbent, thus large mass transfer will be occurred, and therefore large biosorption process will take place [30].

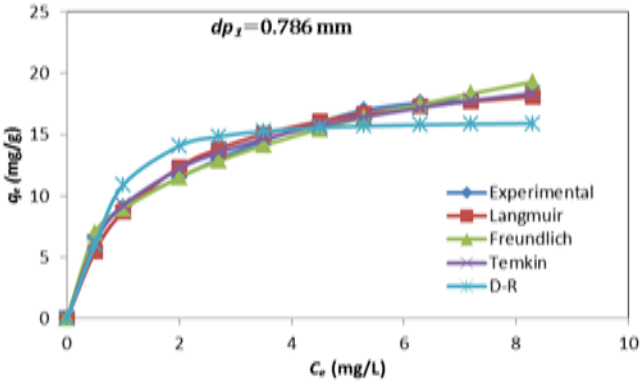

Fig. 12. Comparison between the measured and modelled isotherm curves for biosorption of MB ions onto WF biomass at 298 K, [I.C.=50 mg/L, *p*H=6, biosorbent dose=0.3g, agitation speed=200 rpm, contact time=60 min]

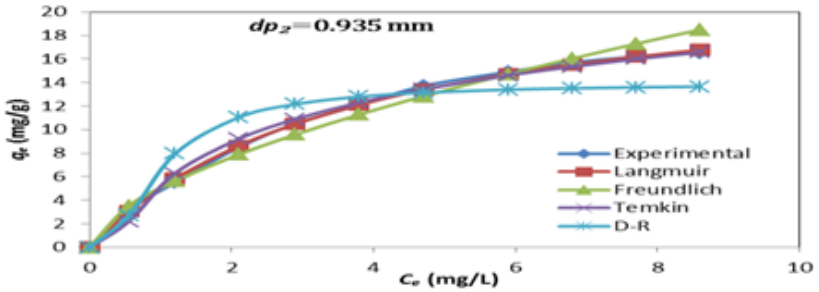

Fig. 13. Comparison between the measured and modelled isotherm curves for biosorption of MB ions onto WF biomass at 298 K, [I.C.=50 mg/L, *p*H=6, biosorbent dose=0.3g, agitation speed=200 rpm, contact time=60 min]

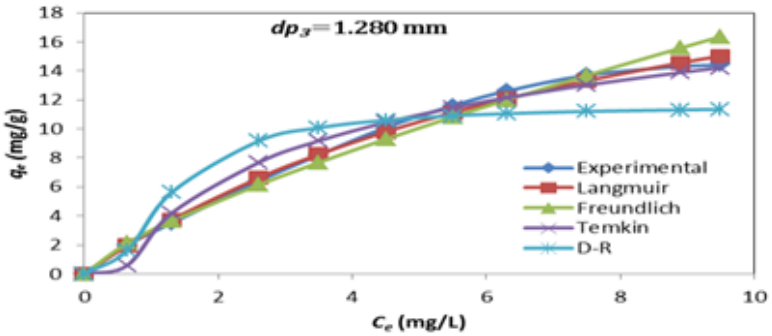

Fig.14. Comparision between the measured and modelled isotherm curves for biosorption of MB ions onto WF biomass at 298 K, [I.C. =50 mg/L, *p*H=6, biosorbent dose=0.3g, agitation

Column studies

Estimation of minimum fluidization velocity

Minimum fluidization velocity (U_{mf}) can be determined by measuring the pressure drop through the bed of biosorbent. Experimentally, the known weight particles of the biosorbent was filled partially in the column, and then mixed strongly with water, after that, the bed was left to stagnant, and then the flow rate was increased gradually. At each increment in flow rate, the pressure drop was recorded by manometer. Initially, the pressure drop rises linearly below the minimum fluidization velocity. By plotting the pressure drops across the bed against the superficial fluid velocity in logarithmic scale, the U_{mf} can be red from the sharp change in the pressure drop.

In fluidized bed, with no channelling, the pressure drop is equal to buoyant weight of particles per unit area. The total fractional force on the particles must equal the effective weight of the bed. Thus the pressure drop across the bed is given by [31]:

$$\Delta p = (\rho_s - \rho_l)(1-\varepsilon).g.h \quad (14)$$

where, ρ_s and ρ_l are the particles density and fluid density (kg/m^3) respectively, ε is the void fraction, g is the gravitational acceleration (9.8 m/s^2), and h is the bed height (m).

In a liquid fluidized bed, the void fraction ε can be calculated theoretically by using Richardsion-Zeki equation [32].

$$\frac{U}{U_l} = \varepsilon^n \tag{15}$$

where, U is the superficial fluid velocity, U_l is the settling velocity of the particle at infinite dilution, and n is an index constant. The index n is a function Reynolds number at terminal velocity (Re_t).

The value of the bed voidage can be found experimentally by the following equation

$$\varepsilon = \frac{V_\varepsilon}{V_b} = \frac{V_b - V_p}{V_b} = 1 - \frac{V_p}{V_b} = 1 - \frac{m_p}{V_b\ \rho_s} = 1 - \frac{m_p}{\rho_s\ A\ h_{mf}} \tag{16}$$

where V_p is the volume of the particle, V_b is the volume of the fluidized bed, $V\varepsilon$ is the volume of the voids, m_p is the mass of the particles (kg), A is the cross-sectional area of the bed (m^2), and h_{mf} is the height of fluidized bed (m).

Ergan equation is used as a correlation for prediction of the minimum fluidization velocity [33], and it is derived from Carman-Kozeny equation as follows:

$$U_{mf} = \frac{U}{d\rho_l} R_e \tag{17}$$

Properties of fluidized-bed

Table 3
THEORETICAL AND EXPERIMENTAL VOIDAGE FOR DIFFERERENT PARTICLE SIZES AT $U=U_{mf}$

Particle size (mm)	U_i (mm/s)	Index (n)	Calculated ε	Experimental ε
1.4-1.18	20	2.78	0.58	0.63
9.92-8.83	18	2.54	0.52	0.59
8.83-7.01	16	2.42	0.45	0.50

Table 4
FLUIDIZATION PROPERTIES OF THREE DIFFERENT SIZE PARTICLES

Particle size (mm)	Mass (g)	Static height (cm)	Δp (pa)	h_{mf} (cm)	Calculated U_{mf} (mm/s)	Experimental U_{mf} (mm/s)
1.4-1.18	20	2.8	66.4	4.5	4.51	4.55
	40	4.1	75.9	7.0		
	60	5.5	102.5	10		
	80	8.3	138.8	15.5		
	100	10.2	145.2	22		
9.92-8.83	20	2.1	51.3	3.7	3.42	3.48
	40	3.4	68.2	6.2		
	60	4.2	92.3	8.8		
	80	7.7	117.1	12.9		
	100	9.3	133.6	19.1		
8.83-7.01	20	1.7	29.8	2.5	2.31	2.37
	40	2.8	54.4	5.5		
	60	3.6	71.7	8		
	80	6.9	84.1	10.5		
	100	7.4	109.5	16		

Effect of bed height

Removal of MB in fluidized bed column by biosorption has a proportional relationship with increasing the quantity of biosorbent in the column, resulting that an increase in bed depth causes an increase in the volume of an aqueous solution with increase in resident time on the bed, thus the quantity of MB removed increased.

Figure 15 shows the breakthrough curves profile of MB biosorption using different bed heights (5, 10, 20 cm) with constant flow rate (3 L/hr). It is clear that the breakthrough time (t_b) and exhaustion time (t_e) are increased with increasing the bed depth. It is noticed that from the interval t_b to t_e, the S-shape curve will be decreased with increasing the bed depth from 5 to 20 cm, which means, the uptake capacity of WF on methylene blue will be increased slightly with increasing the bed height.

This phenomenon will be occurred due to the increase in the surface area of the biosorbent and contact time, also, it can be seen that the exhaustion time will be increased with increasing the bed depth (Z) from 5 to 20 cm.

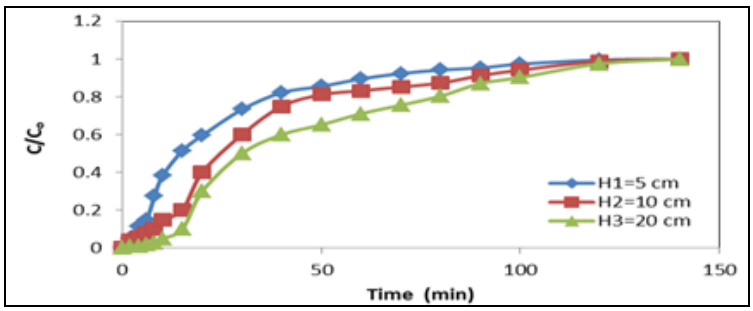

Fig. 15. Effect of bed height on breakthrough curve at 3 L/hr flow rate and 50 mg/L ion concentration, *p*H=6, column diameter=10.2 cm, mean particle size=0.935 mm, temperature=25 °C

Effect of flow rate

From figure 16, it was observed that when an increasing in the flow rates of aqueous dye methylene blue solution, the exhaustion time was decreased, also, the breakthrough curve will be shorter, and then the biosorption capacity per unit time of biosorbent is decreased slightly at the same bed depth. Thus it was considered that the performance of the biosorption process using fluidized bed system is more effective at lower flow rates. The main phenomena here, when the flow rate is increased, the ions of the adsorbate will leave the column without taking a sufficient time to penetrate the pores of biosorbent, causing the earlier breakthrough and exhaustion times and then a steeper breakthrough curve.As a result, in order to get a good contact time, the biosorption process should be made in small flow rates of adsorbate into the column in order to allow the molecules of adsorbate to take more time to enter the pores of biosorbent.

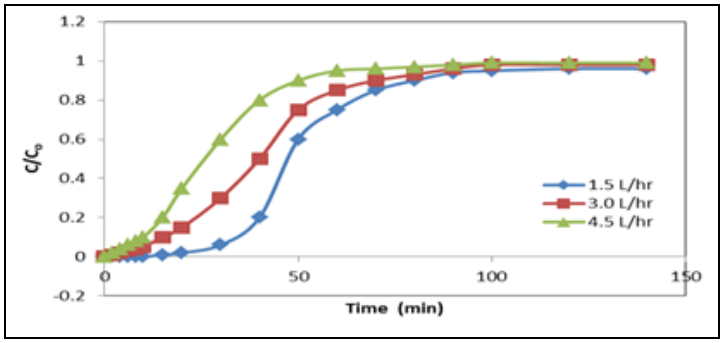

Fig. 16. Effect of flow rate on breakthrough curves at 10 cm bed depth and 50 mg/L ion concentration, *p*H=6, column diameter=10.2 cm, mean particle size=0.935 mm, temperature=25 °C

Effect of initial ion concentration

The effect of initial MB dye concentrations (25, 50, 100 mg/L) on the biosorption of MB at constant bed height of 10 cm and constant flow rate 3 L/hr is shown in figure 17. It can be observed that as the initial MB concentration is increased from 25 to 100 mg/L, the breakthrough and exhaustion time is decreased considerably. In the biosorption of MB by WF, the breakthrough time is decreased from 30 to 20 min and the exhaustion time is decreased from 100 to 80 min, this is due to the fact that high dye concentration leads to quick saturation of the sorbent which in turn leads to the earlier breakthrough and exhaustion time. Also, it can be seen from the same figure that more favourable and steep breakthrough curves were obtained at high influent MB concentration. These results demonstrated that the change in concentration gradient affects the saturation rate and breakthrough time. This can also be explained by the fact that more sorption sites were being filled when the concentration of the dye is increased.

As a result, at higher metal concentration, the driving force of adsorption (the difference between the concentration of solute on the sorbent and concentration of solute in the solution) is greater due to the high concentration difference facilitated by high mass transfer coefficient values. Thus, higher adsorption capacities are achieved at higher metal concentration and the values of mass transfer zone MTZ were observed to be decreased with an increase in the influent MB concentration.

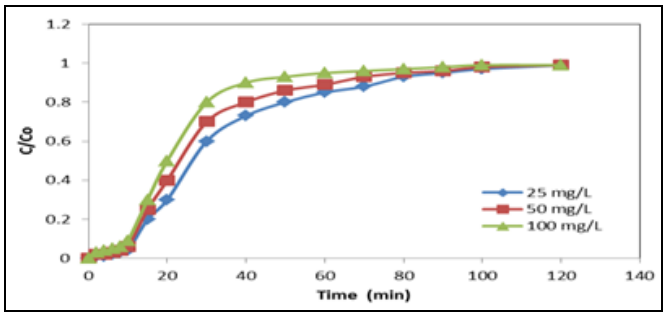

Fig. 17. Effect of initial concentration on breakthrough curves at10 cm bed depth and 3 L/hr flow rate, *p*H=6, column diameter=10.2 cm, mean particle size=0.935 mm, temperature=25 °C

Conclusions

In this study, WF(WF) type (*Agaricus bisporus*) was used as a biosorbent material to remove the Methylene Blue dye from aqueous solution by using two systems, batch and fluidized. Biosorption process was found to be strongly dependent on pH of solution, initial concentration of MB, biosorbent dose and contact time. It was found that the amount of MB biosorbed on waste fugal biomass increases when pH increases in the range of 2 to 6 of the maximum biosorption value of 6. Also it was noticed that the uptake removal will be increased with increasing of the initial concentration of MB in the solution, the optimum contact time was 40 minutes and the best dose used was 0.3 g. Four models have been used to fit the equilibrium biosorption data by Langmuir, Freundlich, Temkin and Dubinin-Radushkevich. It was fitted well in the Langmuir isotherm model gives a monolayer biosorption on a homogeneous surface and the values of separation factor R_L indicate a favorable biosorption. The maximum biosorption capacity of MB was 21.23, 24.154, 28.90 mg/g for a particle size of 0.789, 0.935, 1.280 mm respectively. Temkin and D-R models show that the values of mean free energy E indicate that the biosorption of MB onto WF biomass was donated by physisorption process. Fluidized bed experiments have shown that uptake removal was a strong function of initial flowrate, bed height and initial ion concentration. The uptake removal increases rapidly with increasing in the fluidized bed and initial concentration, while decreases with increasing in the flow rates. The fluidized bed can be used effectively in the treatment of wastewater. As a result, this study shows that a WF biomass can be effectively used as a potential biosorbent for MB dye removal from aqueous solutions and the data obtained from the batch experiments are useful to design fixed and fluidized bed biosorption columns.

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